

# Radiation synthesis and characterization of 3-(trimethoxysilyl) propyl methacrylate silanized silica-graft-vinyl imidazole for Hg(II) adsorption

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**Abstract** Silica-based adsorbent was prepared by radiation induced grafting of vinyl imidazole (VIM) onto the silanized silica, which was silanized by 3-(trimethoxysilyl) propyl methacrylate. The effects of monomer composition and absorbed dose on the grafting yield were investigated to optimize the reaction conditions. The results showed that a VIM concentration of  $2.5 \text{ mol} \cdot \text{dm}^{-3}$  and an absorbed dose of 50 kGy were the optimal reaction conditions. FT IR and XPS spectra manifested that VIM was successfully grafted onto the silica surface. The SS-g-VIM adsorbent had excellent selectivity for Hg(II) adsorption in mixture divalent cationic metal solution and a maximum adsorption capacity of ca. 78 mg/g to Hg(II) at pH 5. The adsorption isotherm was investigated and the adsorption of Hg(II) fitted well with Langmuir mode. These results suggested that SS-g-VIM adsorbent has potential application for the removal of Hg(II) from wastewater.

**Key words**  $\gamma$  Radiation, Grafting, Silica, Vinyl imidazole, Adsorbent

## 1 Introduction

The contamination by mercury in water sources is an important environmental concern as it is an extremely toxic metal that can cause irreversible neurological damage to human<sup>[1]</sup>. Poly(*N*-vinyl imidazole) and its copolymer hydrogels were found to be capable of chelating a large varieties of metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{UO}_2^{2+}$  and so on<sup>[2-5]</sup>. Therefore, the absorbent functionalized with poly(*N*-vinyl imidazole) is expected to be useful for the removal of  $\text{Hg}^{2+}$  from wastewater. Silica is chemically inert and has excellent mechanical properties. The surface modification by reaction of the surface silanol groups makes it a eximious adsorption base material<sup>[6,7]</sup>. 3-(trimethoxysilyl) propyl methacrylate, which is widely used as a carbonyl source<sup>[8,9]</sup>, was used to modify the surface of the silica<sup>[10]</sup>. Graft polymerization is effective to prepare adsorbents with desired ion-exchange and

chelating capacity to certain target, which can be initiated by using gamma rays, electron beams (EB), UV, plasma treatment, and chemical initiators.

In our previous work, DMAEMA was grafted onto silica matrix by radiation grafting using  $\gamma$ -rays and electron beams (EB), revealing the potential of synthesized silica-based adsorbents for the application of heavy-metal-ion removal from wastewater. The adsorbents show privilege on the adsorption of heavy metal ions, such as Cr(VI), As(V) and Hg(II), especially in strong acidic environment<sup>[11]</sup>. AAM/VIM was cogenerated onto chlorotrimethylsilane (TMCS) silanized silica by pre-radiation grafting using electron beam (EB) successfully<sup>[12]</sup>.

In this work, VIM was grafted onto 3-(trimethoxysilyl) propyl methacrylate silanized silica by radiation-induced grafting. The effects of reaction conditions, such as monomer composition and absorbed dose, were investigated to optimize properties of the adsorbent. The properties concerning

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the Hg(II) adsorption, such as selective adsorption of Hg and adsorption isotherm, were to be investigated.

## 2 Experimental

### 2.1 Materials

Column chromatography silica gel (particle size 0.15–0.30 mm, average pore size 10 nm, Branch of Qingdao Haiyang Chemical Co. Ltd., China) was used as the substrate. 3-(trimethoxysilyl) propyl methacrylate and VIM (>98%) was purchased from Sinopharm Chemical Reagent Co., Ltd., China and used without purification. Other chemicals used were analytical reagent (AR).

### 2.2 Preparation of the adsorbent

The silica was backwashed with  $1.0 \text{ mol} \cdot \text{dm}^{-3}$   $\text{HNO}_3$  at  $70^\circ\text{C}$  to remove impurities. After washed by distilled water and dried in vacuum at  $80^\circ\text{C}$ , the silica (5.0 g) was silanized with 5.0 g 3-(trimethoxysilyl) propyl methacrylate in 80 mL xylene at  $80^\circ\text{C}$  for 72 h. The unreacted trimethylchlorosilane was cleaned by xylene. Silanized silica was dried in vacuum at  $60^\circ\text{C}$ .

Silanized silica (SS) and VIM aqueous solution were sealed in polyethylene bags purged with nitrogen gas. The samples were irradiated to desired absorbed dose by  $\gamma$ -rays at room temperature with a dose rate of  $300 \text{ Gy} \cdot \text{min}^{-1}$ .

The homopolymer and unreacted monomer were removed by distilled water and ethanol. Finally, the SS-g-VIM adsorbent was dried in vacuum at  $50^\circ\text{C}$ .

### 2.3 Characterization of the adsorbent

#### 2.3.1 Grafting yield

Grafting yield (GY) of the samples was determined by mass method. The grafting yields were calculated using Eq.(1).

$$GY = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

where  $W_1$  is the weight of SS-g-VIM,  $W_0$  is the initial weight of silanized silica.

#### 2.3.2 FT IR

FT IR analyses of the SS and SS-g-VIM were performed in a Fourier Transform Infrared Spectroscopy (NICOLET750) with MCT/A attachment. The

spectra were measured in transmittance mode at a wave number range of  $4000\text{--}600 \text{ cm}^{-1}$ .

#### 2.3.3 XPS

The X-ray photoelectron spectroscopy (XPS) analysis was performed with an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al  $K\alpha$  radiation (225 W, 15 mA, 15 kV) and low energy electron flooding for charge compensation. To compensate for surface charges effects, binding energies were calibrated using C 1s hydrocarbon peak at a binding energy (BE) of 284.80 eV. The data were converted into VAMAS file format and imported into CASAXPS software package for manipulation and curve fitting.

### 2.4 Hg(II) adsorption behavior

#### 2.4.1 Adsorption experiment

For selective adsorption, aqueous solutions of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  mixture with each concentration of 100 ppm were prepared. Around 30 mg adsorbent was immersed in 50 mL adsorbate with continuously stirring for 8 h. The pH of the solution was adjusted by  $\text{HNO}_3$ .

For Hg(II) adsorption, around 30 mg adsorbent was immersed in 50 mL of Hg(II) solution with continuously stirring for 8 h.

#### 2.4.2 Adsorption capacity

The adsorption capacity of metal ions per unit weight of adsorbent at time  $t$ ,  $q_t$  ( $\text{mg} \cdot \text{g}^{-1}$ ), was calculated from the mass balance by Eq.2.

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

where  $C_0$  is the initial concentration of adsorbate ( $\text{mg} \cdot \text{L}^{-1}$ ),  $C_t$  is the concentration of adsorbate at time  $t$  ( $\text{mg} \cdot \text{L}^{-1}$ ),  $V$  is the volume of the adsorbate, and  $m$  is the mass of the adsorbent.

#### 2.4.3 Measurement of metal ions concentration

For selective adsorption, the concentration of various heavy metal ions in the supernatant was measured by the Inductively Coupled Plasma-Atomic Emission Spectrometer (PROFILE SPEC, Leeman, USA).

For Hg(II) adsorption, the concentration of Hg(II) was measured by colorimetry using a UV-Vis Spectrophotometer (UV-3010, Hitachi, Japan)<sup>[13]</sup>. 1mL of the sample solution or diluted sample solution was added to beakers and their pH was adjusted to 2 by

$\text{HNO}_3$  for the formation of the mercury–dithizone complex. A saturated solution of dithizone in ethanol (9 mL) was then added, and the solutions were allowed to equilibrate for 1 min before recording the absorbance at 495 nm. The calibration curve was measured using  $\text{Hg(II)}$  standard solution from 5 ppm to 40 ppm under the same experiment conditions.

### 3 Results and discussion

#### 3.1 Optimization of reaction condition

The effects of reaction conditions, i.e. absorbed dose and monomer composition, on the grafting yield of SS-g-VIM were investigated to obtain an optimal reaction condition for the preparation of adsorbent. The dose rate of  $300 \text{ Gy} \cdot \text{min}^{-1}$  was adopted for the grafting reaction.

##### 3.1.1 Effect of absorbed dose

Figure 1 shows the effect of absorbed dose on the grafting yield of SS-g-VIM. VIM concentration was fixed to  $1.5 \text{ mol} \cdot \text{L}^{-1}$ . The monomer grafted successfully onto SS at a low initial adsorbed dose of 10 kGy. The grafting yield increased with the increment of absorbed dose. When the absorbed dose increased to 70 kGy, the grafting yield reached ca. 23%. However, the increment of grafting yield was retarded after 50 kGy and certain amount of homopolymer formed when the absorbed dose exceeded 70 kGy so that an absorbed dose of 50 kGy was chosen for further experiment.

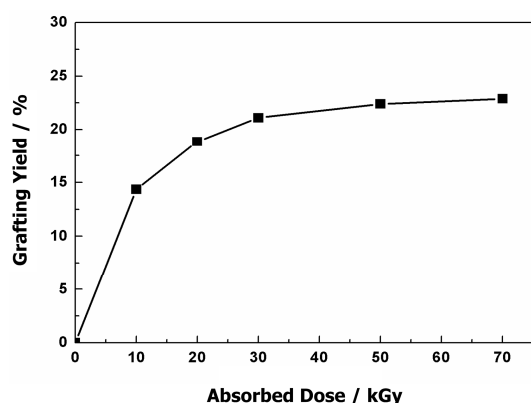


Fig.1 Effect of absorbed dose on the grafting yield.

##### 3.1.2 Effect of monomer composition

The effect of VIM monomer concentration on the grafting yield is shown in Fig.2. The grafting yield increased with the increment of concentration of VIM.

The grafting yield of the adsorbent reached 35% when the concentration of VIM was  $2.5 \text{ mol} \cdot \text{L}^{-1}$ . However, the increment of grafting yield was retarded after  $2.5 \text{ mol} \cdot \text{L}^{-1}$  so that it is not economic to choose a concentration higher than  $2.5 \text{ mol} \cdot \text{L}^{-1}$ .

Therefore, an optimal reaction condition, i.e. an absorbed dose of 50 kGy,  $2.5 \text{ mol} \cdot \text{L}^{-1}$  of VIM, was applied to prepare the adsorbents for further characterization. The grafting yield in this condition was determined as 35 %.

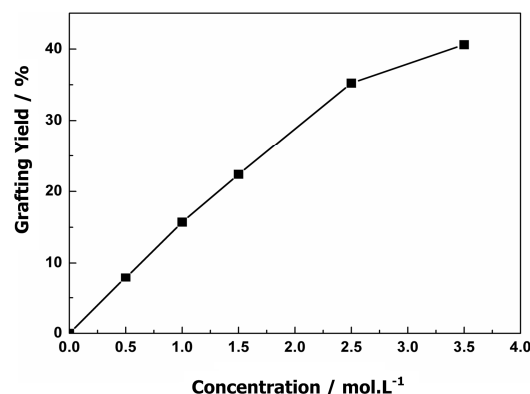


Fig.2 Effect of VIM concentration on the grafting yield.

#### 3.2 Characterization of the adsorbent

##### 3.2.1 FT IR analysis

FT IR spectra of silica and SS-g-VIM are presented in Fig.3.

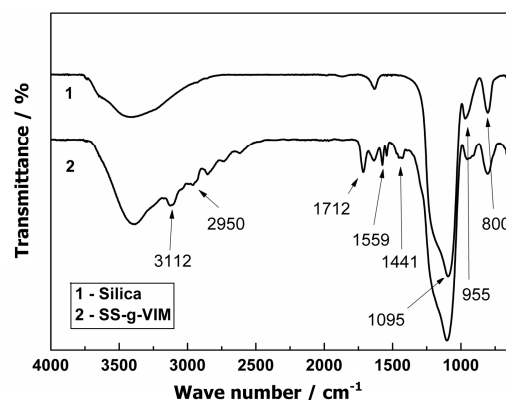


Fig.3 FT IR spectra of silica and SS-g-VIM adsorbents prepared at optimal conditions.

In silica spectra, the characteristic peaks at around 1095, 955 and  $800 \text{ cm}^{-1}$  were ascribed to the asymmetric stretching vibrations of Si-O-Si, stretching vibration of free Si-OH groups on the surface of the amorphous solid and symmetric stretching vibrations of Si-O-Si bonds, respectively<sup>[14]</sup>.

For SS-g-VIM spectra, the peaks at 3 112 and 2950  $\text{cm}^{-1}$  were ascribed to the stretching vibration of the =CH in the ring of VIM and  $\text{CH}_2$  in the backbone, respectively. The absorption bands at 1 712  $\text{cm}^{-1}$  was ascribed to the stretching vibration of the C=O group<sup>[15]</sup>, while the absorption band at 1 417  $\text{cm}^{-1}$  and 1506  $\text{cm}^{-1}$  was ascribed to bending vibration of  $\text{CH}_2$  and the stretching vibration of the C=C and C=N group in VIM<sup>[16]</sup>. The characteristic peaks of VIM appeared in the FT IR spectrum of SS-g-VIM, confirmed that the silica was silanized successfully and VIM has been grafted onto the silanized silica.

3.2.2 XPS analysis

The XPS spectra of SS and SS-g-VIM adsorbents are illustrated in Fig.4. The appearing of N1s peak suggested that VIM has been grafted onto the silanized silica successfully<sup>[17]</sup>. Considering the binding energy, Si 2p and O 1s existed in the same situation before and after grafting, which indicating that the grafting reaction has little effect on the backbone of silica and silanol groups, and the reaction occurred with - $\text{CH}_2$ -free radical generated from alkyl group of silanization reagent<sup>[18]</sup>. The results further proved the successfully grafting of VIM onto the silanized silica.

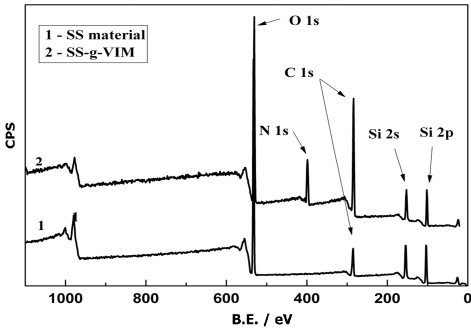


Fig.4 XPS spectra of total elements of silanized silica and SS-g-VIM adsorbents prepared at optimal conditions

3.3 Adsorption behavior of Hg(II)

SS-g-VIM adsorbent prepared in the optimal reaction condition, i.e. an absorbed dose of 50 kGy, 2.5  $\text{mol}\cdot\text{L}^{-1}$  of VIM, was applied to study the adsorption behavior of Hg(II).

3.3.1 Selective adsorption of Hg(II)

Selective adsorption is important for the separation of metal ions from wastewater. Table 1 lists the adsorption capacities of various heavy metal ions in  $\text{HNO}_3$  solution at pH 5. It was found that SS-g-VIM

adsorbent has excellent selectivity for Hg(II) adsorption in mixture divalent cationic metal solution.

3.3.2 Adsorption isotherms

The adsorption behavior of Hg(II) onto SS-g-VIM at pH 5 is shown in Fig.5. The initial concentration of Hg(II) increased from 10 to 200 ppm. The Langmuir isotherm model (E.3) and Freundlich model (Eq.4) were applied to discuss the adsorption mechanism and calculate theoretical maximum adsorption capacity<sup>[19]</sup>.

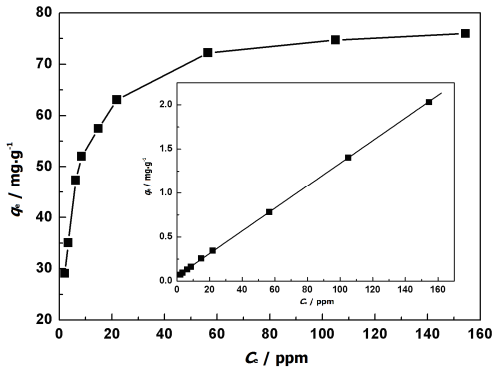


Fig. 5 Adsorption isotherm of Hg(II) onto SS-g-VIM adsorbent.

Table 1 Selectively adsorption of Hg(II) in various divalent heavy metal ions

Metal ions	Cu <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Ni <sup>2+</sup>	Hg <sup>2+</sup>
Recovery/%	0.4	0.5	3.0	0.1	5.6	44.4

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \tag{4}$$

where  $C_e$  is the equilibrium concentration of ions ( $\text{mg}\cdot\text{L}^{-1}$ ) and  $q_e$  is the amount of ions adsorbed by per gram adsorbent ( $\text{mg}\cdot\text{g}^{-1}$ ).  $q_m$  is the theoretical maximum adsorption capacity ( $\text{mg}\cdot\text{g}^{-1}$ ).  $K_L$  is the adsorption energy ( $\text{L}\cdot\text{g}^{-1}$ ), respectively.  $q_m$  and  $K_L$  were calculated from the slope and the intercept of the linear line of  $C_e/q_e$  versus  $C_e$ , respectively.

Table 2 listed the corresponding Langmuir and Freundlich constants and correlation coefficients ( $R^2$ ).

Table 2 Isotherm parameters of the Langmuir model and Freundlich model for the adsorption of Hg(II)

Langmuir			Freundlich		
$q_{\max}$	$K$	$R^2$	$K_f$	$n$	$R^2$
78.00	0.226	0.999	29.35	4.68	0.878

It was found that Langmuir equation fitted the experiment data better than Freundlich equation with a

correlation coefficient of 0.999. This result indicates that the adsorption of Hg(II) ions by SS-g-VIM adsorbent is a monolayer adsorption<sup>[20]</sup>. In the experiment condition (i.e. original Hg(II) in the range of 10–200 ppm), the theoretical maximum adsorption capacity was calculated to be 78 mg·g<sup>-1</sup>.

#### 4 Conclusion

Silica-based adsorbent, namely SS-g-VIM, was prepared by  $\gamma$  radiation induced grafting of vinyl imidazole(VIM) onto the silanized silica, which was silanized by 3-(trimethoxysilyl) propyl methacrylate. The results of thermal analysis, FTIR and XPS manifested that VIM was successfully grafted onto the silica surface. At the optimal reaction conditions, i.e. VIM concentration of 2.5 mol·L<sup>-1</sup> and an absorbed dose of 50 kGy, the grafting yield was determined to be 35%. The SS-g-VIM adsorbent had excellent selectivity for Hg(II) adsorption in mixture divalent cationic metal solution and a considerable Hg(II) uptake of ca. 78 mg·g<sup>-1</sup> at room temperature at pH 5. The adsorption of Hg(II) fitted with Langmuir model, indicating that the adsorption is a monolayer adsorption. The SS-g-VIM adsorbent is expected to be useful for the removal of Hg(II) from waste water.

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